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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

9052-106

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

**TRANSMITTAL LETTER TO THE UNITED STATES  
 DESIGNATED/ELECTED OFFICE (DO/EO/US)  
 CONCERNING A FILING UNDER 35 U.S.C. 371**

**10/049779**

INTERNATIONAL APPLICATION NO.  
**PCT/GB00/03194**

INTERNATIONAL FILING DATE  
**August 18, 2000**

PRIORITY DATE CLAIMED  
**August 18, 1999**

TITLE OF INVENTION

**PROCESS FOR SEPARATING METALS**

APPLICANT(S) FOR DO/EO/US

**Robert Charles THIED, Justine Elizabeth HATTER, Kenneth Richard SEDDON, William Robert PITNER, David William ROONEY,  
 and David HEBDITCH**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☐ Amendments to the claims of the International Application Under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report Under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11 to 20 below concern document(s) or information included:**

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO 1449 and \_\_\_ references.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1 821 - 1.825.
18. ☒ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4)
20. ☒ Other items or information: PCT International Search Report (attached to published international application)

U.S. APPLICATION NO. <b>10/049779</b>		INTERNATIONAL APPLICATION NO <b>PCT/GB00/03194</b>		ATTORNEY DOCKET NO <b>9052-106</b>	
21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a) (1) - (5)).				CALCULATIONS PTO USE ONLY	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....				<b>\$1040.00</b>	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or IPO . . . . .				<b>\$890.00</b>	
International preliminary examination fee 37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....				<b>\$740.00</b>	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....				<b>\$710.00</b>	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) .....				<b>\$100.00</b>	
<b>ENTER APPROPRIATE BASE FEE AMOUNT =</b>				<b>\$890.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e))				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	18 - 20 =	0	x <b>\$18.00</b>	\$	
Independent Claims	1 - 3 =		x <b>\$84.00</b>	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ <b>\$280.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2				\$	
<b>SUBTOTAL =</b>				\$	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f))				\$	
<b>TOTAL NATIONAL FEE =</b>				\$	
Fee for Recording the enclosed assignment (37 CFR 1.21(h)) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +				\$	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$890.00</b>	
				Amount to be refunded:	\$
				charged:	\$

- a. ☒ A check in the amount of **\$890.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 50-0220 in the amount of \$\_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0220. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

*Laura M. Kelley*  
 Laura M. Kelley, Reg No 48,441  
 Date: Feb. 18, 2002



**20792**  
 PATENT TRADEMARK OFFICE

**CERTIFICATE OF EXPRESS MAILING**

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I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to: BOX PCT, Commissioner for Patents, Washington, DC 20231. Attn: DO/PTO/US.

*Susan E. Freedman*  
 Susan E. Freedman

Attorney's Docket No. 9052-106

PATENT

IN THE UNITED STATES DESIGNATED OFFICE (DO/US)

In re: Application of Thied et al.  
Serial No.: To be Assigned  
Filed: Concurrently Herewith  
For: ***PROCESS FOR SEPARATING METALS***

February 18, 2002

BOX PCT  
Commissioner for Patents  
Washington, DC 20231  
Attn: DO/EO/US

**PRELIMINARY AMENDMENT**

Sir:

Prior to the examination of the above application and calculation of claim fees, please amend the above-identified application as follows. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The marked-up version of the changes to the claims is captioned "**Version With Markings To Show Changes Made.**"

**In the Specification:**

On page 1, line 1 after the title of the invention, please insert the following section:

**--CROSS-REFERENCE TO RELATED APPLICATIONS**

The present application claims priority under 35 U.S.C. § 371 from PCT Application No. PCT/GB00/03194 (published under PCT Article 21(2) in English), filed on August 18, 2000 which claims the benefit of Great Britain Application Serial No. 9919496.1, filed on August 18, 1999, the disclosures of which are incorporated by reference herein in their entireties.--

On page 3, line 10, delete the word "STATEMENTS" and insert --SUMMARY-- therefor.

In re: Application of Tried et al.  
Serial No.: To be assigned  
Filed: Concurrently herewith  
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On page 13, line 1, delete the word "**CLAIMS**" and insert the following: --WHAT IS CLAIMED IS:--

**In the Claims:**

Please enter the amended claims as follows:

2. (Amended) A method according to claim 1 wherein the ionic liquid comprises a cation component.

3. (Amended) A method according to claim 2 wherein the cation component comprises an organic cation.

5. (Amended) A method according to claim 1 wherein the anode is selected from a group consisting of halide, nitrate, sulphate, tetrafluoroborate, hexafluorophosphate and tetrachloroaluminate.

6. (Amended) A method according to claim 1 wherein the anode comprises trifluoromethanesulfonate bis(trifluoromethanesulfonyl)imide.

7. (Amended) A method according to claim 1 wherein the ionic liquid is pre-loaded with metal ions.

10. (Amended) A method according to claim 9 wherein the metal chloride comprises AgCl or CdCl<sub>2</sub>.

12. (Amended) A method according to claim 1 further comprising depositing purified metal at the cathode.

13. (Amended) A method according to claim 1 further comprising depositing the metal at the cathode as a compound.

In re: Application of Tried et al.  
Serial No.: To be assigned  
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14. (Amended) A method according to claim 1, wherein the composition to be separated is irradiated nuclear fuel.

15. (Amended) A method according to claim 1, wherein the metal to be separated comprises uranium.

16. (Amended) A method according to claim 1 further comprising purifying the ionic liquid for further use.

Please cancel Claims 17-20.

Please insert the following new Claims 21 and 22:

21. (New) A method according to claim 1 wherein the metal to be separated comprises plutonium.

22. (New) A method according to claim 3 wherein the organic cation is selected from a group consisting of N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium.

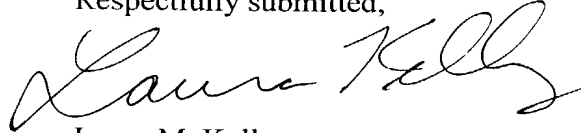
In re: Application of Tried et al.  
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### REMARKS

Applicant respectfully requests consideration of the foregoing amendments. The above claims have been amended to better conform to U.S. practice and to eliminate the multiple dependency of claims.

Please enter this amendment prior to calculating the fee in this case. Applicant respectfully requests substantive examination on the merits.

Respectfully submitted,



Laura M. Kelley  
Registration No. 48,441

### Correspondence Address:



20792

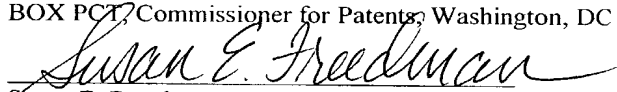
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Susan E. Freedman

Date of Signature February 18, 2002

In re: Application of Tried et al.  
 Serial No.: To be assigned  
 Filed: Concurrently herewith  
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**Version With Markings To Show Changes Made**

**In the Specification:**

On page 1, line 1 after the title of the invention, the following section has been added:

**--CROSS-REFERENCE TO RELATED APPLICATIONS**

The present application claims priority under 35 U.S.C. § 371 from PCT Application No. PCT/GB00/03194 (published under PCT Article 21(2) in English), filed on August 18, 2000 which claims the benefit of Great Britain Application Serial No. 9919496.1, filed on August 18, 1999, the disclosures of which are incorporated by reference herein in their entireties.--

**In the Claims:**

The claims have been amended as follows:

2. (Amended) A method according to claim 1 wherein [the cation component of] the ionic liquid comprises a cation component [is an organic cation].

3. (Amended) A method according to claim 2 wherein the cation component comprises an organic cation [is N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium].

5. (Amended) A method according to [any of the preceding claims] claim 1 wherein the [anion component is] anode is selected from a group consisting of halide, nitrate, sulphate, tetrafluoroborate, hexafluorophosphate [or] and tetrachloroaluminate.

6. (Amended) A method according to [any claims 1 to 4] claim 1 wherein the [anion component is] anode comprises trifluoromethanesulfonate bis(trifluoromethanesulfonyl)imide.

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7. (Amended) A method according to [any of the preceding claims] claim 1 wherein the ionic liquid is pre-loaded with metal ions.

10. (Amended) A method according to claim 9 wherein the metal chloride [is] comprises AgCl or CdCl<sub>2</sub>.

12. (Amended) A method according to [any of the preceding claims wherein] claim 1 further comprising depositing purified metal [is deposited] at the cathode.

13. (Amended) A method according to [any of the preceding claims wherein] claim 1 further comprising depositing the metal [is deposited] at the cathode as a compound.

14. (Amended) A method according to [any of the preceding claims] claim 1, wherein the composition to be separated is irradiated nuclear fuel.

15. (Amended) A method according to [any of the preceding claims] claim 1, wherein the metal to be separated [is] comprises uranium [and/or plutonium].

16. (Amended) A method according to [any of the preceding claims wherein, after use in the method, the ionic liquid is purified for further use] claim 1 further comprising purifying the ionic liquid for further use.

Claims 17-20 have been canceled.

Claims 21 and 22 have been added.

21. (New) A method according to claim 1 wherein the metal to be separated comprises plutonium.



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22. (New) A method according to claim 3 wherein the organic cation is selected from a group consisting of N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium.

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**PROCESS FOR SEPARATING METALS****FIELD OF THE INVENTION**

5 This invention relates to processes for the separation of metals from compositions containing metals. The invention includes processes for the treatment of spent nuclear fuel forming part of a process for reprocessing, conditioning and/or partitioning nuclear fuels. Reference will be made hereinafter mainly to nuclear fuels but it should be understood that the invention is not restricted to any particular type of material and has application outside the nuclear industry.

10

**BACKGROUND OF THE INVENTION**

15 In the metals recovery and refining industry generally, the type of metal recoverable from a solvent is dependent upon the size of the electrochemical window of the solvent in which the metal is dissolved, and from which purification and recovery is taking place. In aqueous solutions, this is governed by the electrochemical window of water or supporting electrolyte. This limits the recovery, purification and electroplating of metals on to surfaces from aqueous solution to those metals whose electrode reduction potentials are more positive than the cathodic limit of the aqueous solution. In acidic aqueous solution, metal ions would not be recoverable where their electrode reduction potentials are more negative than that of the  $\text{H}_3\text{O}^+$  ION. Recovery of metals with electrode reduction potentials more negative than  $\text{H}_3\text{O}^+$ , means that non-aqueous (aprotic) solvents are required. There are a number of aprotic solvents which are used. There are a number of non-protic solvents which are used. These are often molten salts and, for instance, aluminium is industrially purified electrochemically by electrolysis of  $\text{Al}_2\text{O}_3$  dissolved in molten cryolite  $\text{Na}_3\text{AlF}_6$ . Other aprotic media include the organic solvents, such as acetonitrile, benzene and toluene.

25 There exists two well developed processes which use molten salts for the reprocessing of irradiated nuclear fuel. The Argonne National Laboratory electrometallurgical treatment (ANL - EMT) process and the Dimitrovgrad State

Scientific Centre, Research Institute of Atomic Reactors (SSC – RIAR) process both use molten salts at high temperatures (773 and 1000K respectively). The ANL process treats the spent nuclear fuel by a process called electrefining in which current flow is used to oxidise a uranium anode to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as uranium metal. The SSC – RIAR process uses chemical oxidants (chlorine and oxygen gases) to react with powdered  $UO_2$  fuel to form higher oxidation state compounds such as  $UO_2Cl_2$  which are soluble in the molten salt. At the cathode the uranium compounds are reduced to  $UO_2$ , which forms a dendritic deposit.

The disadvantage of these processes is that these molten salts are typically mixtures of salts which are liquid only at high temperatures and this causes inherent disadvantages in a reprocessing plant, in particular, as a result of the challenges posed in the engineering of the process and the materials of construction.

Ionic liquids free of molecular solvents were first disclosed by Hurley and Wier in a series of US patents (24446331, 2446339, 2446350). In general terms an ionic liquid is a salt, a mixture of salts, or a mixture of components which produce a salt or a mixture of salts, which melts below or just above room temperature. (As used herein, the term "salt" means an entity comprising entirely of cationic and anionic species). Such liquids are known as "ionic liquids" although this term is sometimes used for salts which melt at relatively high temperatures. In this specification, the term "ionic liquid" refers to a salt which melts at a temperature of up to 100°C.

Co-pending patent application PCT/GB99/00246 discloses a method for reprocessing spent nuclear fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid to substantially separate fissile material from other components of irradiated fuel. Also disclosed is the subsequent treatment of the resulting ionic liquor, either by solvent extraction or electrochemical treatment to recover the dissolved uranium and plutonium.

Whilst the methods described in PCT/GB99/00246 are suitable for general use and, in particular, for use in nuclear fuel reprocessing, it has previously been thought that an electrorefining process, which avoids the need for an initial chemical dissolution step, requires the use of a high temperature molten salt electrolyte. If fuel is  
5 chemically oxidatively dissolved, there is less control over the species which are dissolved during this step. All those species which will be oxidised by the oxidising agent added will enter into the solution. Because the oxidising agents and conditions are aggressive, most species will dissolve except for species such as the noble metals.

## 10 STATEMENTS OF INVENTION

According to the present invention there is provided a method for separating a metal from a composition including said metal, the method comprising forming an electrolytic cell having an anode, a cathode and an electrolyte, the anode comprising a composition including said metal and the electrolyte comprising an ionic liquid,  
15 applying a sufficient potential difference between the anode and the cathode to cause the metal to transfer from the anode to the cathode and be deposited thereon.

Ionic liquids offer the ability to broaden the electrochemical window of the solvent in which the metal is dissolved, and from which purification or recovery is taking place.

20 Ionic liquids have advantages over molten salts. As they operate at closer to ambient temperatures, they are probably less aggressive towards construction components, and engineering and process costs are likely to be less. They also have advantages over organic solvents such as acetonitrile, in being non-volatile, with consequent environmental benefits. Furthermore, metal species are usually more soluble in ionic  
25 liquids than in organic solvents.

Ionic liquids can be used to electrodeposit metals which are generally considered to be electropositive, for example, metals whose electrode reduction potentials are more positive than the  $\text{H}_3\text{O}^+$  ion. An ionic liquid can be used for this task if there are  
30 benefits of using ionic liquids over aqueous based solutions. An example is the

electroplating industry (for instance silver) where there are safety and environmental benefits of using ionic liquids rather than cyanide ion solutions.

Using an electrolytic cell in which the electrolyte is an ionic liquid and the anode is the metal composition to be separated, application of a suitable potential difference results in electrochemical oxidation of the metal at the anode, causing it to enter into the ionic liquid electrolyte medium. The soluble metal species is then electro-transported to the cathode where a reduction process occurs. These results are surprising because, previously, molten salts were the only materials with a sufficiently large electrochemical window for an electrochemical process requiring large potential differences, and the temperature at which the process was performed was dictated by the melting temperature of the salt. Ionic liquids provide large electrochemical windows at ambient temperatures.

Preferably the cation component of the ionic liquid is an organic cation, for instance, a nitrogen heterocycle such as N-substituted pyridinium (preferably alkylpyridinium, for instance, N-butylpyridinium), N,N'-disubstituted imidazolium (preferably N,N'-dialkylimidazolium, for instance, 1-ethyl-3-methylimidazolium), and substituted ammonium and phosphonium, for instance, tetraalkylammonium (for instance, tetraoctylammonium) or tetraalkylphosphonium (for instance, tributyltetradecylphosphonium).

The substituents are preferably hydrocarbyl and more preferably alkyl, which may be branched. The hydrocarbyl (e.g. alkyl) groups usually contain from 1 to 18 carbon atoms and some usually from 1 to 8 carbon atoms.

The cation may therefore preferably be a disubstituted imidazolium ion where the substituent groups take the form  $C_nH_{2n+1}$  for  $1 \leq n \leq 8$ , and the substituent groups are linear or branched groups. In preferred disubstituted imidazolium ions one substituent has  $n=1, 2, 3$  or  $4$  (of which methyl is particularly preferred) and the other has  $n=2, 3, 4, 5, 6, 7$  or  $8$  (of which octyl, hexyl and more particularly butyl are

preferred, linear groups being preferred). Alternatively, the cation might be a substituted tetraalkylammonium or tetraalkylphosphonium ion, where the alkyl groups take the form of  $C_nH_{2n+1}$  for  $1 \leq n \leq 6$ , and are linear or branched groups. Preferred examples include tetrabutylammonium and tetrabutylphosphonium.

5 However, the alkyl groups are preferably of different lengths resulting in asymmetrical substitution. Alternatively, the cation might be a substituted pyridinium ion, where the substituent group also takes the form  $C_nH_{2n+1}$  for  $1 \leq n \leq 8$ , and the substituent groups are linear or branched groups; suitable substituents include butyl, 2-(2-methyl)propyl, 2-butyl and octyl but straight chain alkyl, especially butyl,

10 is preferred.

The ionic liquid may be a mixture of two or more ionic liquids, which together provide the desired properties such as, for instance, a lower viscosity. An example is a mixture of disubstituted imidazolium in which the components of the mixture have

15 alkyl groups of different lengths, e.g. a mix of 1-octyl-3-methylimidazolium chloride ([emim]Cl) and 1-ethyl-3-methylimidazolium chloride ([omim]Cl).

The anion component is likely to be an inorganic species such as halide (for instance, chloride), nitrate, sulphate, tetrafluoroborate, hexafluorophosphate or

20 tetrachloroaluminate, triflate which is trifluoromethanesulfonate ( $CF_3SO_3^-$ ), and bistriflylimide which is bis(trifluoromethanesulfonyl)imide ( $[(CF_3SO_2)_2N]^-$ ).

Preferably the ionic liquid will be pre-loaded with metal ions, in order that the electrorefining process can be initiated. Such pre-loading may be achieved by, for

25 example, the addition to the ionic liquid of a soluble uranium salt or a salt such as cadmium chloride. Addition of a metal salt, such as cadmium chloride, results in the reaction of this metal salt with uranium metal, creating metal ions in the solution.

Pre-loading with uranium ions may also be achieved by displacement of a metal

30 chloride, such as AgCl or Cd Cl<sub>2</sub>. Alternatively, pre-loading with uranium ions may be achieved by destructive reduction of the electrolyte. At the anode uranium is



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In a preferred embodiment of the invention irradiated nuclear fuel feed in the form of metal is placed within an anode basket. The anode basket is then immersed within an ionic liquid, together with a suitable cathode, such as a stainless steel mandrel. Through the application of a suitable potential difference between the anode and  
5 cathode, uranium metal will be electrochemically oxidised at the anode, and enter into the ionic liquid electrolyte medium. The soluble uranium species will then be electro-transported to the cathode, where a reduction process occurs. Contaminants with more positive reduction potentials than uranium will remain unoxidised in the anode basket. Similarly, contaminants with more negative reduction potentials than  
10 uranium will remain unreduced in solution.

Electro-reduction of the soluble uranium species should result in the deposition of uranium metal (or a uranium compound) at the cathode. Provided that a suitable oxidising potential is applied at the anode and a suitable reduction potential is  
15 applied at the cathode, uranium or a uranium compound will be deposited at the cathode in a purified form.

The ionic liquid contains fission product compounds and compounds of the actinide elements which are oxidised from the cathode with the uranium and must be stripped  
20 of these contaminants before its subsequent re-use. This may be achieved by any one or a combination of a number of different routes. Selected fission products and actinides such as plutonium can be electrochemically extracted through the application of a suitable potential using a liquid metal cathode such as a mercury electrode. Alternatively, dissolved plutonium may be co-deposited on the cathode  
25 with the uranium, irrespective of whether the metals are deposited in the metallic state (in the (0) oxidation state), as complexes or as oxides. Such co-deposition is useful in the manufacture of mixed oxide fuels.

Selective deposition of a metal from a solution containing its ions is well known in  
30 the art and does not require detailed explanation here. However all metal ions in a solution will have different electrode reduction potentials to reduce the ions to a



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lower positive valency, or to reduce them to zero valency. Electrode reduction potentials are dependent upon the element, the oxidation state of the ion in the solvent and to the presence of other ions or molecules. If a potential is applied across a solution then all metal ions with a more positive potential will be deposited on the cathode. Metal ions with a more negative potential will remain in solution. Once a particular ion has been removed from the solution, the electrode can be removed and replaced with a new one, biased at a slightly more negative potential, for the deposition of the next metal with a more negative reduction potential. If it is desired to deposit two metals together, then a potential more negative than the reduction potential for both ions is applied.

Certain organic cations are selected for the ionic liquid, to give extremely low reduction potentials. The lower the "cathodic window" of the solvent, the greater the range of species which can be removed from solution by electroreduction. For example, imidazolium cations give at least a 1 volt advantage over aqueous solutions.

Fission products may alternatively or additionally be removed from the ionic liquid by the addition of an organic solvent. Addition of an organic species results in the precipitation of fission product compounds. The precipitate can be filtered from the ionic liquid and calcined to convert to oxide prior to a vitrification step. Cleaned ionic liquid can then be recycled to the electrorefiner.

In order to maximise process rate the electro-refining equipment is engineered to minimise anode to cathode distance and the cathode deposit is removed and collected. The latter step also prevents electrical shorting between the anode and cathode due to the growth of metallic dendrites.

The invention will now be further described with reference to the following examples. In each case the reference electrode was immersed in a 0.1 Molar solution of silver nitrate in [bmim] NO<sub>3</sub>, separated from the bulk solution in a glass tube with a porous Vycor tip.

Example 1: anodisation of a uranium electrode in [bmim]NO<sub>3</sub> at room temperature

An electrochemical cell was set up with a separated platinum coil counter electrode, a Ag reference electrode, a uranium metal plate working electrode and [bmim]NO<sub>3</sub> (1-butyl-3-methylimidazolium nitrate) as electrolyte. Electrolysis was carried out by applying a potential of +0.6V to the uranium electrode. After the passage of 1000 Coulombs, the uranium electrode was removed and weighed. The weight loss of the uranium (0.78g) indicated that the uranium species required 3.2 equivalents per mole, indicating the production of a U(III) species.

10

Example 2: electrorefining uranium in [heim]Cl at 70°C

Due to the viscosity of [heim]Cl 1-hexyl-3-ethylimidazolium nitrate chloride, this work was carried out at 70°C. A solution of U(III) was produced in [heim]Cl as by electrolysis of a uranium electrode at +0.3 V. This is anodic dissolution of the uranium metal, as in Example 1. Comparison of the charge passed (1235 Coulombs) with the weight loss of the uranium electrode (1.012 g) gives a charge to mass balance of 3.0 eqv/mol, indicating the production of a U(III) species. The platinum counter electrode used in the preparation of this solution was then replaced with a copper wire immersed in the U(III) solution. Electrolysis was carried out at an applied potential of -1.6 V to the copper cathode; the uranium metal electrode served as the anode. A total of 236 Coulombs was passed during the electrolysis. The weight gain of the cathode electrode was only 18.7 mg compared to the 193 mg weight loss of the uranium anode. This clearly shows that uranium has been electrotransported from the anode to the cathode, the current efficiency being only about 10%. Material which settled on the bottom of the cell indicated that deposited uranium does not adhere well to copper. The charge to mass loss of the uranium electrode (236 C/193 mg = 3.0 eqv/mol) indicated that even while acting as a counter electrode, the species produced through anodisation is still U(III).

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Example 3: voltammetry of U(III) in [emim]Cl at 80°C

7.99g [emim] Cl was melted at 80°C. A solution containing 0.03mol L<sup>-1</sup> (U(III)) was produced by the anodiation of a uranium rod (Q<sup>TM</sup>111C) as in Example 1. Cyclic voltammograms were recorded in the resulting solution at a glassy carbon electrode.

- 5 A typical voltammogram is shown in Figure 1. The oxidation of U(III) to U(IV) occurs at potentials greater than *ca.* -0.2V versus Ag(I)/Ag. This process is irreversible, as demonstrated by the large difference in the anodic and cathodic potentials (-0.06 and -1.07 V, respectively). The reduction of U(III) to U metal occurs at potentials less than *ca.* -1.5V.

10

This example thus shows the potential at which uranium (III) is reduced to metal, and shows that uranium can be purified from other metals, such as plutonium, by an electrochemical means.

15 Example 4: anodiation of Pu(III) in [emim]Cl at 90°C

An electrochemical cell was set up with a separated platinum coil counterelectrode, a Ag reference electrode, and a plutonium metal rod working electrode. Electrolysis was carried out by applying a potential of -1.5V to the plutonium electrode. After the passage of 27.5C, the plutonium electrode was removed and weighed. A direct  
20 comparison of the weight loss of the plutonium (80mg) with the charge passed would erroneously indicate that the plutonium species generated was Pu(II). However, it was noted that plutonium metal in contact with the ionic liquid reacts spontaneously; the bright metal quickly forms a dark layer of corrosion products as the metal undergoes oxidation and the ionic liquid cation undergoes reduction. This is most  
25 likely because the reduction potential of Pu(III) is more negative than that of the 1-ethyl-3-methylimidazolium cation (*ca.* -2.2V). Therefore, given the known chemistry of plutonium in chloride media, it is most likely that the species generated during electrolysis is Pu(III); the excess weight loss is due to spontaneous corrosion.

- 30 This example shows evidence that plutonium can anodically dissolve into an ionic liquid, and that the oxidation state is probably Pu(III).



Example 6: precipitation of fission products from [hmim]Cl using an organic solvent

Europium(III) chloride ( $\text{EuCl}_3$ ) was used to simulate fission products dissolved in an ionic liquid. 4.66g [hmim]Cl and 1.05g  $\text{EuCl}_3$  were dissolved in  $20\text{cm}^3$  dry acetonitrile. This solution was heated to  $70^\circ\text{C}$  under reflux in a dry dinitrogen atmosphere for 3 hours and allowed to cool. After approximately 30 minutes in a refrigerator, fine white crystals had precipitated. 1.81g of precipitate were collected. The results of elemental analysis of the crystals were 41.04% carbon, 6.86% hydrogen, and 9.22% nitrogen. The theoretical composition of the complex [hmim]<sub>3</sub>[EuCl<sub>6</sub>] ( $\text{C}_{30}\text{Cl}_6\text{EuH}_{57}\text{N}_6$ , RAM =  $866.50\text{ g mol}^{-1}$ ) is 41.58% carbon, 6.63% hydrogen and 9.70% nitrogen which suggests that this is the identity of the precipitate.

This Example shows that fission products dissolved within an ionic liquid can be recovered by the addition of an organic solvent.

## CLAIMS

1. A method for separating a metal from a composition including said metal, the method comprising forming an electrolytic cell having an anode, a cathode and an electrolyte, the anode comprising a composition including said metal and the electrolyte comprising an ionic liquid, applying a sufficient potential difference  
5 between the anode and the cathode to cause the metal to transfer from the anode to the cathode and be deposited thereon.
2. A method according to claim 1 wherein the cation component of the ionic liquid  
10 is an organic cation.
3. A method according to claim 2 wherein the organic cation is N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium.  
15
4. A method according to claim 3 wherein the organic cation includes alkyl groups which are linear or branched and not all of the same chain length.
5. A method according to any of the preceding claims wherein the anion component  
20 is halide, nitrate, sulphate, tetrafluoroborate, hexafluorophosphate or tetrachloroaluminate.
6. A method according to any claims 1 to 4 wherein the anion component is trifluoromethanesulfonate bis(trifluoromethanesulfonyl)imide.  
25
7. A method according to any of the preceding claims wherein the ionic liquid is pre-loaded with metal ions.
8. A method according to claim 7 wherein the ionic liquid is pre-loaded with metal  
30 ions by the addition of a soluble uranium salt.

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9. A method according to claim 7 wherein the ionic liquid is pre-loaded with uranium ions by displacement of a metal chloride.
- 5 10. A method according to claim 9 wherein the metal chloride is AgCl or CdCl<sub>2</sub>.
11. A method according to claim 7 wherein the ionic liquid is pre-loaded with uranium ions by destructive reduction of the electrolyte.
- 10 12. A method according to any of the preceding claims wherein purified metal is deposited at the cathode.
13. A method according to any of the preceding claims wherein the metal is deposited at the cathode as a compound.
- 15 14. A method according to any of the preceding claims wherein the composition to be separated is irradiated nuclear fuel.
15. A method according to any of the preceding claims wherein the metal to be separated is uranium and/or plutonium.
- 20 16. A method according to any of the preceding claims wherein, after use in the method, the ionic liquid is purified for further use.
- 25 17. A process for the reprocessing of spent nuclear fuel, the process including a method of any preceding claim.
18. Use of an ionic liquid in the electrefining of a composition to separate a metal therefrom.
- 30 19. Use according to claim 18 wherein the composition is spent nuclear fuel.

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9919496.1 18 August 1999 (18.08.1999) GB(71) Applicant (for all designated States except US): **BRITISH NUCLEAR FUELS PLC** [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB).

(72) Inventors; and

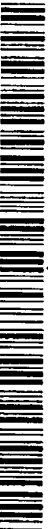
(75) Inventors/Applicants (for US only): **THIED, Robert,** Charles [GB/GB]; British Nuclear Fuels Plc.-Research & Technology, Sellafield Works, Seascale, Cumbria CA20 1PG (GB). **HATTER, Justine, Elisabeth** [GB/GB]; British Nuclear Fuels PLC, Risley, Warrington, Cheshire WA3 6AS (GB). **SEDDON, Kenneth, Richard** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road, Belfast BT9 5AG (GB). **PITNER, William, Robert** [GB/GB]; Questor Centre, Queens University, David Keir Building, Stanmillis Road, BelfastBT9 5AG (GB). **ROONEY, David, William** [GB/GB], Questor Centre, Queens University, David Keir Building, Stanmillis Road, Belfast BT9 5AG (GB). **HEBDITCH, David** [GB/GB]; BNFL Magnox Generation, Berkeley, Gloucestershire GL13 9PB (GB).(74) Agent: **HARRISON GODDARD FOOTE;** Tower House, Merrion Way, Leeds LS2 8PA (GB).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**Published:**

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(54) Title: PROCESS FOR SEPARATING METALS

(57) Abstract: A method for separating a metal from a composition including the metal involves forming an electrolytic cell in which the anode comprises a composition including the metal. The electrolyte is an ionic liquid. A sufficient potential difference is applied between the anode and the cathode to cause the metal to transfer from the anode to the cathode and to be deposited thereon.

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Figure 1

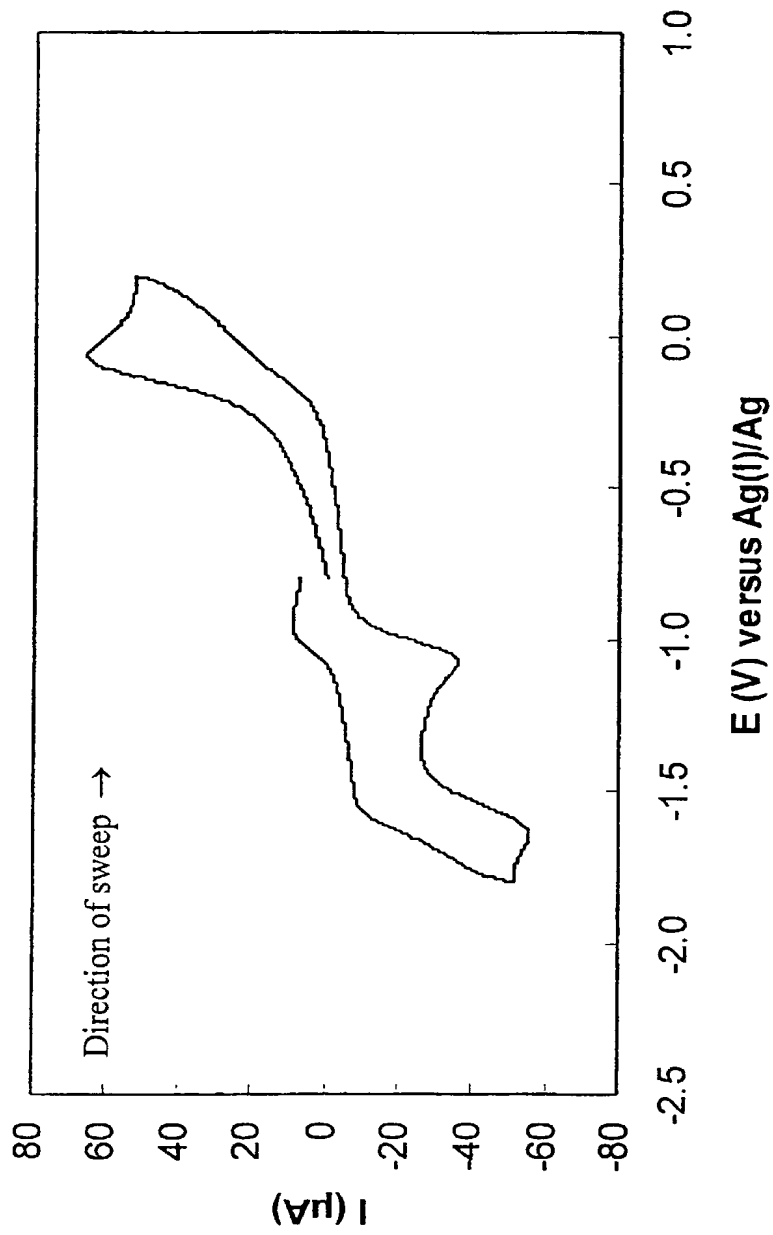
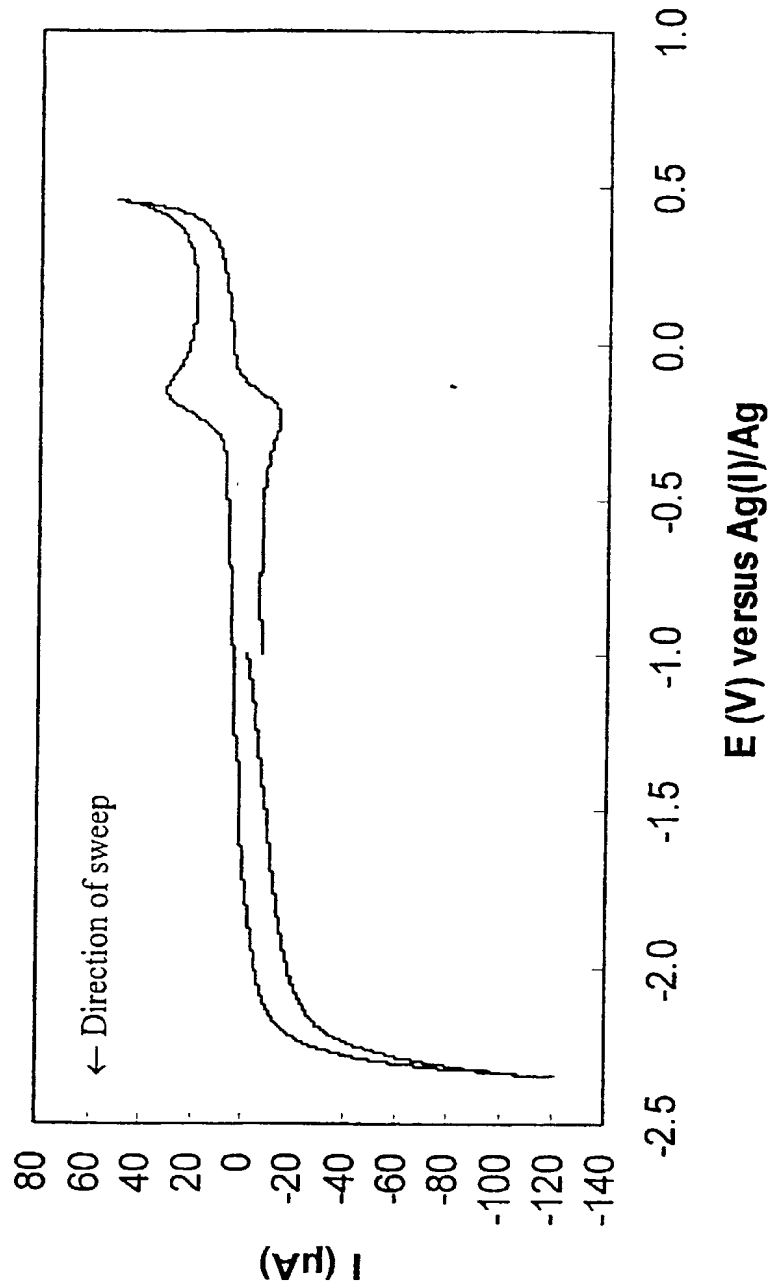


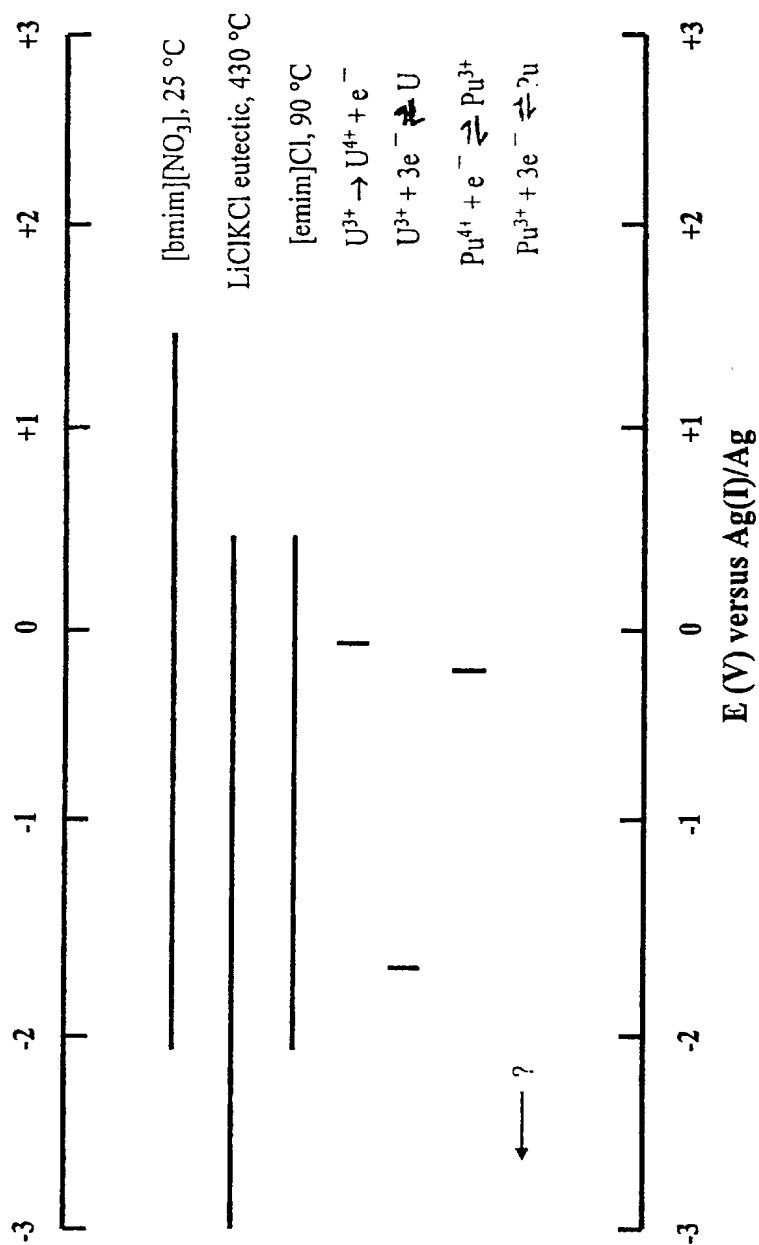
Figure 2



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Figure 3



# DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

Attorney Docket No. 9052-106

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

the specification of which

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OR

☒ was filed on February 18, 2002 as United States Application No. or PCT International Application Number (10/049,779 ) and was amended on \_\_\_\_\_ (if applicable). I hereby authorize and request Myers, Bigel, Sibley & Sajovec, P.A. to insert above in parenthesis the U.S. application number assigned to the application which claims priority in International Application No. PCT/GB00/03194 when known.

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I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56, including material information that became available between the filing date of the prior application and the National or PCT International filing date of the continuation-in-part application, if applicable.

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PCT/GB00/03194	PCT	August 18, 2000	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
Number	Country	MM/DD/YYYY Filed	Priority Claimed
9919496.1	Great Britain	August 18, 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
Number	Country	MM/DD/YYYY Filed	Priority Claimed

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)
Application Number(s)	Filing Date (MM/DD/YYYY)

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Appln. Serial No.	Filing Date	Status Patented/Pending/Abandoned
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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## Customer Number:



20792

PATENT TRADEMARK OFFICE

Send correspondence to:

## Customer Number:



20792

PATENT TRADEMARK OFFICE

Direct telephone calls to:

(919) 854-1400

Facsimile:

(919) 854-1401

Full name of (first/sole) inventor:

1-00

Robert Charles THIED

Inventor's

Signature:

Robert Charles Thied

Date:

23rd April 2002

Residence:

SEASCALE, CUMBRIA, GREAT BRITAIN GBNCitizenship: BRITISH.

Mailing Address:

SELLAFIELD WORKS, SEASCALE, CUMBRIA  
LA20 1PG, GREAT BRITAIN.

Full name of second inventor:

Justine Elizabeth HATTER

Inventor's

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Residence:

Citizenship:

Mailing Address:

**Customer Number:**



**20792**

PATENT TRADEMARK OFFICE

Send correspondence to:

**Customer Number:**



**20792**

PATENT TRADEMARK OFFICE

Direct telephone calls to:

(919) 854-1400

Facsimile:

(919) 854-1401

Full name of (first/sole) inventor: Robert Charles THIED

Inventor's

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Residence:

Citizenship:

Mailing Address:

Full name of second inventor: 200 Justine Elizabeth HATTER

Inventor's

Signature: Justine Elizabeth Hatter Date: 30/4/2002

Residence: CHESHIRE, GREAT BRITAIN GBN

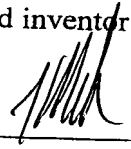
Citizenship: BRITISH

Mailing Address: RISLEY, WARRINGTON, CHESHIRE, WA3 6AS, GREAT BRITAIN

3-00  
Full name of third inventor:

Kenneth Richard SEDDON

Inventor's

Signature: 

Date: 22/5/02

Residence: UK

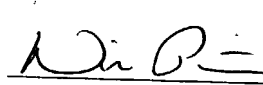
Citizenship: BRITISH

Mailing Address: SCHOOL OF CHEMISTRY, QUEEN'S UNIVERSITY  
DAVID KEIR BUILDING  
STRANMILLIS ROAD  
BELFAST BT9 5AG, N. IRELAND GBS

Full name of fourth inventor:

4-00 William Robert PITNER

Inventor's

Signature: 

Date: 22/04/02

Residence: UK

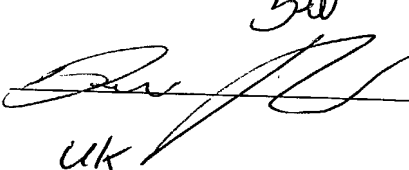
Citizenship: USA

Mailing Address: School of Chemistry  
Queen's University  
Belfast BT9 5AG

Full name of fifth inventor:

5-00 David William ROONEY

Inventor's

Signature: 

Date: 7/5/02

Residence: UK

Citizenship: IRISH

Mailing Address:

SCHOOL OF CHEMICAL ENGINEERING  
QUEEN'S UNIVERSITY BELFAST  
BELFAST, BT9 5AG GBS



Full name of sixth inventor:

60 DAVID JOHN HEBDITCH  
David HEBDITCH

Inventor's

Signature:

David John Hebditch

Date:

June 11, 2002

Residence:

GREENSIDE, BRADLEY GREEN, WOTTON-UNDER-EDGE, GLOUCESTERSHIRE, ENGLAND GL12 7PP  
ENG

Citizenship:

BRITISH

Mailing Address:

BNFLRUTHERFORD R201RISLEYWARRINGTONCHESHIREWA3 6AS CBH